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(54) **Microsphere coating material**

(57) A method for the manufacture of materials for shoe linings and counter linings comprises applying to a fibrous substrate a coating composition comprising a dispersion of a film-forming polymer, in which are dispersed microspheres which are expansible on heating, subjecting the material in a first heating stage to a temperature at which the film-forming polymer forms a cohesive film but at which the microspheres do not expand, and then subjecting the material in a second heating stage to a temperature at which the microspheres expand and a microcellular structure is developed.

The shoe linings and counter linings manufactured by this method are particularly suitable to the manufacture of linings with a coloured surface which may be sued.

GB 2 217 630

IMPROVED SHOE-LINING MATERIALS AND  
A METHOD FOR THEIR MANUFACTURE

The present invention relates to improvements in  
5 or relating to shoes and the manufacture thereof and is  
especially concerned with materials used in the manufacture  
of shoes which are subject in wear to abrasion, for example  
shoe linings, in particular shoe counter-linings. The term  
"shoe" is used herein to denote outer footwear generally  
10 whether ready for wear or in the course of manufacture.

Many shoes have uppers comprising a outer and a  
lining. In ladies' court shoes, whether the uppers are  
lined all over the inside or not, the counter region often  
has a lining of suitable material known as a  
15 counter-lining. A counter-lining is preferably made of a  
material having a high coefficient of friction with respect  
to the foot and hose of a wearer to assist in retention of  
the shoe on the foot in wear; counter-lining materials  
preferably have a good resistance to abrasion and an  
20 appearance pleasing to the eye of a potential purchaser of  
a shoe in which the counter-lining has been incorporated.

A further requirement which has arisen relatively  
recently, in particular as a result of current fashions, is  
for materials for shoe linings, in particular shoe  
25 counter-linings, to have a coloured surface as hereinafter  
defined, and it may be desired that this coloured surface  
should be combined with a sueded surface.

Prior art linings are known which may be produced  
with a sueded surface and, of these, the lining materials  
30 which are manufactured by impregnating a non-woven fibrous  
base material with an aqueous dispersion comprising  
carboxylated rubber, a curing system for the rubber and a  
vinyl chloride polymer resin, drying the impregnated  
material and curing the carboxylated rubber, followed where  
35 required by sueding off of the surface, have proved to be  
particularly successful.

The materials which are manufactured by this method are particularly suitable for the production of shoe linings and counter linings in pastel colours. The base materials are formed from white or light coloured fibres, typically polypropylene/polyester polymers, which inevitably pastellise the product, and this effect becomes particularly marked when the surface is sueded.

An object of the present invention is to provide a method for the manufacture of materials for shoe linings and counter linings, which may optionally have a coloured surface and which may optionally be produced with a sueded surface while retaining the coloured surface where this is provided.

The present invention provides a method for the manufacture of materials for shoe linings and counter linings which method comprises applying to a fibrous substrate a coating composition comprising a dispersion of a film-forming polymer, in which are dispersed microspheres which are expansible on heating, subjecting the material in a first heating stage to a temperature at which the film-forming polymer forms a cohesive film but at which the microspheres do not expand, and then subjecting the material in a second heating stage to a temperature at which the microspheres expand and a microcellular structure is developed.

The present invention further provides materials for shoe linings and counter linings, which materials are manufactured by a method which comprises applying to a fibrous substrate a coating composition comprising a dispersion of a film-forming polymer, in which are dispersed microspheres which are expansible on heating, subjecting the material in a first heating stage to a temperature at which the film-forming polymer forms a cohesive film but at which the microspheres do not expand, and then subjecting the material in a second heating stage

to a temperature at which the microspheres expand and a microcellular structure is developed.

The method according to the invention is preferably a method for the manufacture of materials for shoe linings and counter linings which have a coloured surface as herein defined, in which the coating composition applied to the substrate further comprises a pigment.

The materials for shoe linings and counter linings manufactured by the method according to the invention preferably have a coloured surface as herein defined, and are manufactured by a method which comprises applying to the fibrous substrate a coating composition which further comprises a pigment.

By the term "coloured surface" as used herein, is meant a surface which is pigmented to give a colour which is not pastellised by the effect of white or light-coloured fibres which are present in the fibrous substrate and which affect the appearance of the surface of the lining.

The fibrous substrate to be used in the method according to the invention preferably comprises a bonded non-woven or spun bonded fabric. Suitable materials for the fibres include polypropylene/polyester polymers.

The film-forming component applied to the substrate preferably comprises an aqueous dispersion of a film-forming polymer. Suitable dispersions include latices and aqueous polyurethane dispersions.

Where the film-forming component is applied in the form of an aqueous dispersion, the first heating stage is a drying stage and is suitably carried out at a temperature below 100°C, preferably below 90°C at which temperature the microspheres are not expanded. Expansion of the wet coating should be avoided, as the final coating is more uniform if the coating is dried first. The dried and unexpanded coating is subsequently heated in the second heating stage to a temperature at which the microspheres

are expanded, preferably above 120°C, more preferably 140° to 150°C.

Where the material is required to have a sueded surface, the expanded coating is sueded, for example with  
 5 emery paper, to produce a level surface, with exposed fine cell structure, which surface has a uniform, matt and intense colour.

Suitable methods by which the composition used according to the invention can be coated onto the substrate  
 10 include, in particular, knife coating, for example with a knife on a roll, or rotary screen printing. If rotary screen printing is used, it is helpful to position a smoothing blade after the screen head to remove any pattern left by the screen.

15 During the expansion stage of the method according to the invention, that is the second heating stage, there is a possibility that the base material will curl along its length, so that stentering is necessary. This tendency for curling, and the consequent need for  
 20 stentering, is removed if the expansion stage is carried out on a drum, for example a Fleissner drum.

The invention will now be further described with reference to the following specific examples:-

Example 1

25 A coating system having the following composition was stirred and then milled in a colloid mill to disperse the microspheres:

		<u>Parts by Weight</u>	
		<u>Wet</u>	<u>Dry</u>
30	Nitrile Latex 8250	14,000	5,600
	PVC Latex 7151	6,000	3,540
	Black Pigment Dispersion	800	200
	30% Expancel 461 WU	3,066	919
	10% Viscalex HV30	1,470	147
35	DB 110 (50%) Antifoam	25.3	12.6

Nitrile Latex 8250 is a cross-linkable carboxylated nitrile rubber supplied by Bayer A.G.

PVC Latex 7151 is a polyvinyl chloride latex supplied by Polysar.

- 5 Expancel 461 WU is an expansible microsphere material in wet unexpanded form, supplied by Nobel Industries, Sweden.

Viscalex HV30 is a polyacrylic thickening agent supplied by Allied Celloids Ltd.

- 10 DB 110 is a silicone antifoam agent supplied by Dow Corning.

Immediately before use, the following components were stirred into the coating system:

		<u>Parts by Weight</u>
15	0.5% .880 Ammonia	127
	5.9% Beetle Resin 338	1,495
	5% Viscalex HV30 (10%)	1,270

- 20 Beetle Resin 338 is a melamine formaldehyde condensate supplied by BIP Chemicals, and was used to cross-link the carboxylated nitrile rubber.

The ammonia was added to solubise the HV30 polyacrylic acid thickening agent.

- 25 The viscosity of the latex/Expancel blend after the final additions and stirring was 25,000 to 30,000cps when measured on a Brookfield viscometer, spindle 6, speed 10.

The coating blend was coated onto a bonded non-woven fabric substrate, 0.5mm thick, using a Meyer bar.

- 30 The substrate was coated at a coating weight of 140 to 170gm per square metre and dried at 90°C. At this temperature, the coating dried without expansion of the microspheres. After drying, the thickness of the coated material was from 0.60 to 0.65mm.

- 35 The coated substrate was then heated at 140° to 150°C for 1 to 2 minutes, to expand the microspheres. The

gauge increased to 1.1 to 1.2mm. The expanded material was then heated for a further 5 minutes, to cure the nitrile rubber and develop optimum abrasion resistance. The material was finally sanded to a gauge of 0.8mm.

5           The resultant material had intense surface colouration, uniform thickness and a sanded surface, with good abrasion resistance.

Example 2

10           A coating system having the following composition was stirred and then milled in a colloid mill to disperse the microspheres:

		<u>Parts by Weight</u>	
		<u>Wet</u>	<u>Dry</u>
	Nitrile Latex 2890	250	100
15	30% Expancel 461 WU	33.3	10
	Black Pigment Dispersion	10	2.5
	10% Viscalex HV 30	50	5
	DB 110 (5%) Antifoam	0.5	0.03

20           Just prior to coating, the following curing ingredients were added:

		<u>Parts by Weight</u>	
		<u>Wet</u>	<u>Dry</u>
	0.88 Ammonia (as required)		
25	50% Sulphur Dispersion 2012	4	2
	50% Zinc Oxide Dispersion 2097	6	3
	50% ZDC Accelerator Dispersion 12	2	1
	50% ZMBT Accelerator 1831	2	1
30	Beetle Resin 338	18.75	14.1
	10% Viscalex HV 30	69	6.9

The Nitrile Latex 2890 is supplied by Bayer A.G. and the Sulphur 2012, Zinc Oxide 2097, ZDC 12, and ZMBT 1831 are  
35 supplied by Rubber Latex Ltd.

The viscosity of the latex/Expancel blend after the final additions and stirring was 25,000 to 30,000cps. when measured on a Brookfield viscometer, spindle 6, speed 10.

5           Coating, drying and heating were then carried out as described in Example 1. The gauge increased to 1.1 to 1.2mm. Final curing was carried out as in Example 1. The material was finally sueded to a gauge of 0.8mm.

10           The resultant material had intense surface colouration, uniform thickness and a sueded surface with good abrasion resistance.

#### Example 3

15           The procedure of Example 2 was repeated, with the variation that the 100 parts by weight dry of Nitrile Latex 8250 was replaced by 75 parts by weight dry of Nitrile Latex 2890 and 25 parts by weight of Nitrile Latex 8250.

20           As compared to the coating produced according to Example 2, this material had slightly increased surface coating hardness.

#### Example 4

25           The procedure of Example 1 was repeated, with the variation that the Nitrile Latex used in Example 1 was replaced by 5600 parts by weight dry of Doverstrand Revinex 5043, a styrene - butadiene - acrylonitrile prepolymer latex.

          The resultant material had intense surface colouration, uniform thickness and a sueded surface with good abrasion resistance.

#### 30           Example 5

          A coating system having the following composition was stirred and then milled in a colloid mill to disperse the microspheres:



		<u>Parts by Weight</u>	
		<u>Wet</u>	<u>Dry</u>
	Permatex EX4844 PU dispersion	250	87.5
	Permatex UA9048 Crosslinker	7.5	5.25
5	30% 551 Expancel	33.3	10
	Coloured pigment dispersion	10	2.5
	PB110(5%) Antifoam	0.5	0.03
	0.88 Ammonia (as required)		
	10% Viscalex HV30	50	5

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Permatex EX4844 and UA9048 are supplied by Stahl Chemicals Ltd.

Coating was carried out as described in Example 1, and the coated substrate was dried at 60 or 70°C.

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The coated substrate was then blown at 120°C, at which temperature the microspheres were expanded and the polyurethane completely cured.

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CLAIMS:-

1. A method for the manufacture of materials for shoe linings and counter linings, which method  
5 comprises applying to a fibrous substrate a coating composition comprising a dispersion of a film-forming polymer, in which are dispersed microspheres which are expansible on heating, subjecting the material in a first heating stage to a temperature at which the film-forming  
10 polymer forms a cohesive film but at which the microspheres do not expand, and then subjecting the material in a second heating stage to a temperature at which the microspheres expand and a microcellular structure is developed.

15 2. A method as claimed in Claim 1, in that the substrate comprises a bonded non-woven or spun bonded fabric.

3. A method as claimed in Claim 1 or Claim 2 in  
20 which the coating composition further comprises a pigment.

4. A method as claimed in any of Claims 1 to 3 which further comprises the step of sueding the surface.

25 5. A method as claimed in any of Claims 1 to 4 in which the microspheres are dispersed in an aqueous dispersion.

6. A method as claimed in any of Claims 1 to 5  
30 in which the microspheres are dispersed in a latex or an aqueous polyurethane dispersion.

7. A method as claimed in any of Claims 1 to 6  
in which the material is heated in the first heating stage  
35 to a temperature below 100°C.

8. A method as claimed in Claim 7 in which the material is heated in the first heating stage to a temperature below 90°C.

5 9. A method as claimed in any of Claims 1 to 8 in which the material is heated in the second heating stage to a temperature above 120°C.

10 10. A method as claimed in Claim 9 in which the material is heated in the second heating stage to a temperature of from 140 to 150°C.

11. A material for shoe linings and counter linings which has been manufactured by a method as claimed  
15 in any of Claims 1 to 10.

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